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THE OCCURRENCE OF HARMONICS IN THE INFRA-RED ABSORPTION SPECTRA OF DIATOMIC GASES

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The study of the infra-red absorption bands of gases has within the last few years received a great impetus through Bjerrum's[1] explanation of their structure as the result of the superposition of the molecular rotations on the vibrational motion of the charged atoms, which is the primary cause of the absorption. Bjerrum's suggestion was quickly followed by the discovery of v. Bahr[2] that these bands are, in reality, clusters of comparatively narrow lines, corresponding to the discrete angular velocities predicted for the molecular rotations by the older form of the quantum theory. In a recent number of the *Physical Review*[3] Kemble has called attention to the fact that if the energy of the vibrational motion also takes on only the quantum values the corresponding infra-red absorption bands in the spectra of diatomic gases ought to be accompanied by faint harmonics. An examination of the literature showed only one case, viz., carbon monoxide, in which more than one band was known to exist and this was a faint one at very nearly half the wave length of the fundamental. The present article is a preliminary report on an experimental search for similar harmonics in the infra-red absorption spectra of other diatomic gases and an examination of their structure. First harmonics have been found in the spectra of hydrochloric acid and hydrobromic acid and their structure as well as that of the faint carbon monoxide band has been shown to be in general agreement with the theory. Search was also made for possible second and third harmonics in the spectra of carbon monoxide and hydrochloric acid, but without result.

Apparatus and Method of Procedure.—The work was done on a prism spectrometer with a combination Wadsworth-Littrow mounting similar to that described by Gorton.[4] This arrangement gives an unusually high resolving power by a double passage of the energy through the prism. The energy was measured with a thermopile. The prism was of quartz, the refractive indices given by Carvallo and Rubens[5] being used in computing the wavelength scale. The absorption tube was 78 cm. long and had a minimum inside diameter of 3.5 cm. The ends were closed with windows of fused quartz.

Each galvanometer deflection with the absorption tube in place was 'sandwiched' between two deflections with the tube drawn to one side.

In this manner a curve was obtained, showing the transmission of the tube relative to an air path of equal length. The absorption in the gas was computed by comparing the transmission curve for the tube when evacuated with that when filled with the gas under investigation. From two to six complete sets of observations were taken at each spectrometer setting.

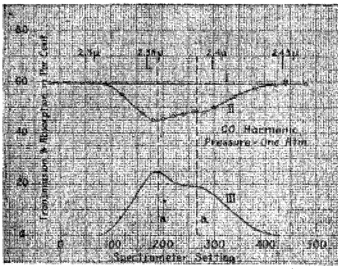

FIG. 1.

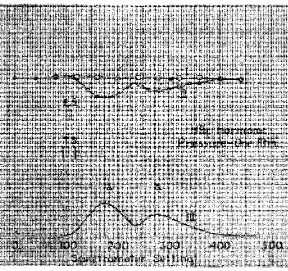

FIG.

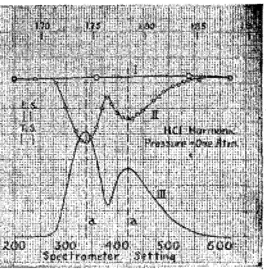

FIG. 3.

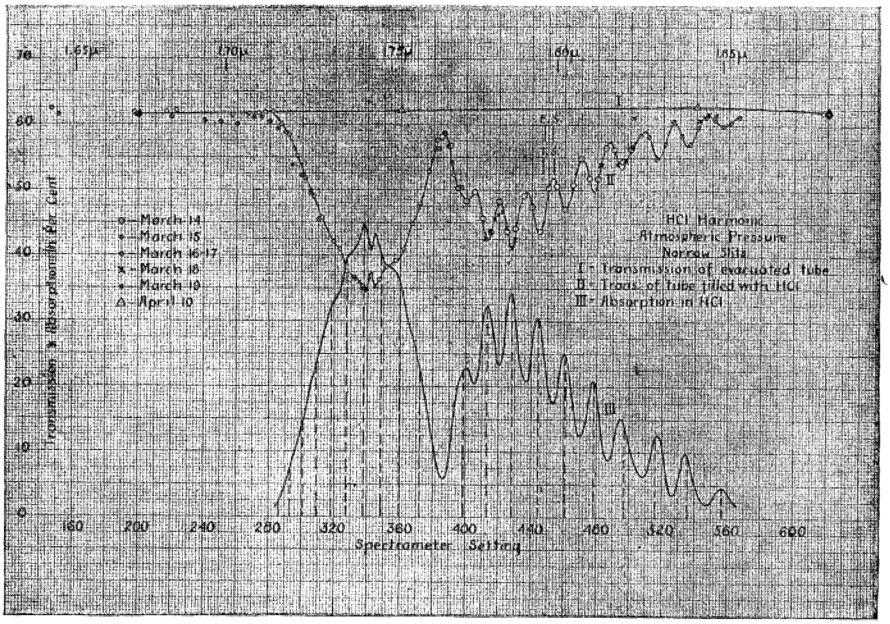

FIG. 4.

Carbon Monoxide.—According to Burmeister[6] the principal infra-red absorption band of CO is a doublet whose maxima are at 4.60 μ and 4.72 μ. The center of the harmonic should accordingly be at 2.33 μ. It should be a doublet with one fourth the wavelength difference between the maxima that is observed in the fundamental. Figure 1 shows the absorption curve obtained. When this curve was taken the spectrometer was not properly adjusted to give its full resolving power. However, it is easy to see that the band is actually a doublet and that within the limits of error of our observations the separation of the maxima of the components is that predicted. The vertical lines *a-a* in the figure have the wavelength separation predicted for the maxima from Burmeister's observations on the fundamental. On the other hand, the wavelength of the center of the band is greater than it should be by 0.043 μ.

This band had previously been observed by Coblentz, Burmeister, and others, but had not been resolved into its two components.

Hydrobromic Acid.—Burmeister gives only one absorption band in the infra-red absorption spectrum of HBr, viz., a doublet with maxima, (corrected for slit-width by the Paschen-Runge formula) at 4.013 μ and 3.836 μ. The center of the harmonic should be at 1.962 μ and the separation of the maxima should be 0.0442 μ. Figure 2 shows the absorption curve obtained. The widths of the entrance slit and thermopile slit are indicated by two pairs of short vertical lines marked E. S. and T. S. respectively. The distance between the maxima is in satisfactory agreement with the theoretical distance (cf. vertical lines *a-a*). As in the case of CO the wavelength of the center of the band is greater than that expected, the error being 0.026 μ.

Hydrochloric Acid.—The infra-red absorption spectrum of HCl consists, according to Burmeister, of a single doublet with maxima (corrected for slit-width) at 3.394 μ and 3.557 μ. We have found an additional doublet (fig. 3) with maxima at 1.783 μ and 1.742 μ. As in the cases of the other gases examined the observed wavelength of the center of the band is somewhat greater than it should be if the band is a true harmonic of the one at 3.475 μ, but the separation of the maxima agrees with the theoretical value predicted from Burmeister's observations.

Figure 4 shows this same HCl band as observed with narrower slits. The quantum lines discovered by v. Bahr in the fundamental are resolved on the long wavelength side of the band but not on the short wavelength side. The reason for the asymmetry in the positions of the quantum lines will be discussed below.

Figure 5 shows the fundamental as observed when the tube was filled with a mixture of air and HCl, the latter having a partial pressure of 20.3 cm. The absolute magnitudes of the absorption shown by this curve have not been determined as accurately as we hope to determine them in the future, but the positions of the bands are probably to be relied on. The wavelength of the center of this band is less than that observed by Burmeister with a prism by 0.01 μ.

Discussion.—According to the theory previously referred to,[3] the infra-red absorption spectrum of a diatomic gas at moderate temperatures should consist of a relatively strong fundamental doublet accompanied by a faint harmonic. The latter band should also be a doublet and the wavelength difference of the components should be one fourth of the wavelength difference of the components of the fundamental. The theory applies to five gases, viz., CO, NO, HCl, HBr, and HI. Of these we have examined three, and in each case the prediction of the theory has been verified. The only discrepancy between theory and observation consists in a slight excess in the observed wavelengths of the 'harmonics' over their computed values, amounting to 0.043 μ, 0.026μ, and 0.025 μ, in the cases of CO, HBr, and HCl respectively.

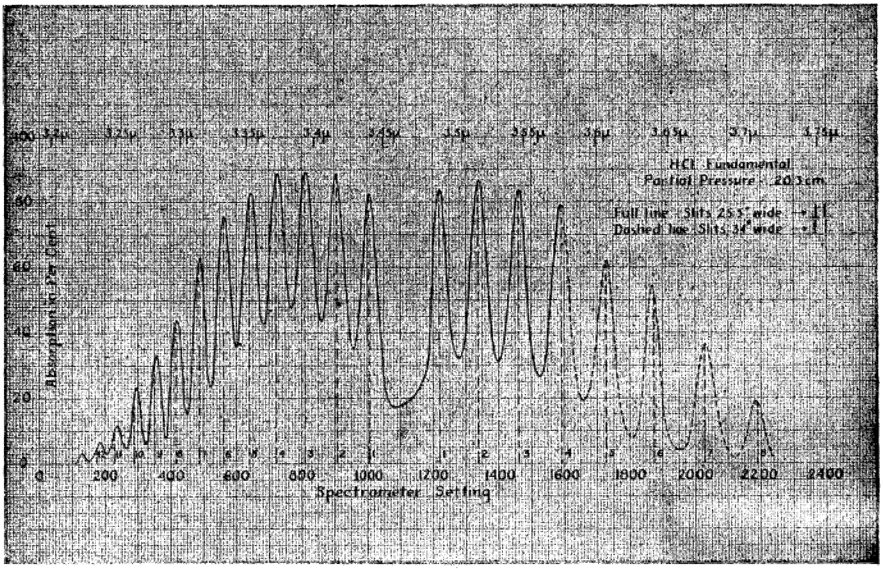

FIG.

This disagreement may be attributed to a slight error in the dispersion curves on which the wavelength measurements are based. As no absorption bands other than those here mentioned are known in the near infra-red spectra of the gases investigated, it seems out of the question that the occurrence of these weak bands at wavelengths so near the computed values can be a matter of chance. Moreover, as these diatomic molecules have but one vibrational degree of freedom, it would be difficult to explain the occurrence of two absorption bands in the infra-red spectra of these gases except as the result of the non-simple harmonic character of motion of the two atoms along their line of centers. That the faint bands are not due to impurities is proved by the spacing of the maxima of the two components. We therefore look upon the small wave length discrepancy referred to as an indication of a slight error in the accepted values of the infra-red refractive indices of quartz.

The Asymmetry of the Bands.—According to the elementary theory of the structure of the infra-red absorption bands of diatomic gases given by Bjerrum[1], the curve obtained when absorption coefficients are plotted against frequency should be a symmetric doublet, of which each half should have the form of the distribution function for angular velocities. He assumes implicitly that the frequency of the atomic vibration is independent of the angular velocity of the molecule. The observed absorption bands are all asymmetric, however, the high frequency component being narrower and more intense. In an unpublished paper read before a recent meeting of the American Physical Society by Kemble[7], it was suggested that this asymmetry might be due to the fact that the frequency of the atomic vibration is lowered by the expansion of the molecule under the influence of the centrifugal force produced by the molecular rotation. This change of frequency would cause a crowding together of the quantum lines in the high frequency component and a corresponding increased separation in the low frequency component. On the basis of this theory the frequency of vibration should be

$$\nu = \nu_0 - a\nu_r^2$$

where a is a constant, ν_0 is the frequency of vibration for zero angular velocity, and ν_r is the frequency of rotation. Combining this assumption with the quantum theory we obtain the following formula for the positions of the two elementary lines corresponding to the pth unit of angular velocity.

$$\acute{\nu} = \nu_0 \pm p\nu_1 - ap^2\nu_1^2.$$

ν_1 is the unit of angular frequency. The dashed vertical lines on figure 4 indicate the theoretical positions of the quantum lines in the HCl harmonic as computed by the above formula, using the values 3.7×10^{-14} and 6.32×10^{11} for a and ν_1 respectively. The vertical lines in figure 5 give the corresponding positions for the fundamental, using the values 2.55×10^{-14} and 6.32×10^{11} for a and ν_1. In each case the agreement is satisfactory.

The unit of angular frequency, ν_1, is inversely proportional to the moment of inertia of the molecule and v. Bahr interpreted an apparent decrease in the value of ν_1, for the larger values of p which was observable on her absorption curve for the HCl fundamental, as an indication of an increase in the moment of inertia with increasing angular velocity. It will be observed that our observations show no perceptible variation in the value of ν_1.

One difficulty arises in connection with this theory of asymmetry. If the faint HCl band is a true harmonic of its strong companion the constant *a* should have twice the value for the former that it does for the latter. According to our observations the ratio of the two values of the constant is about 1.5 instead of 2. However, a very slight change in the assumed form of the dispersion curve in the neighborhood of 3.5 μ would suffice to bring the observations on the two bands into agreement. As a matter of fact the shape of the dispersion curve in this region is somewhat uncertain, for the points determined by Rubens are far apart and slightly irregular. The wavelength scale shown in figure 5 was obtained by drawing the best possible *smooth* curve through the points given by Rubens.

Kinetic Energy at the Absolute Zero.—Figures 4 and 5 emphasize an extremely important fact already evident in v. Bahr's absorption curve for the HCl fundamental, viz., the absence of a central band corresponding to a group of molecules having zero angular velocity. This observation forces the conclusion that none of the molecules are without rotational energy and brings us to a combination of the first form of Planck's quantum theory with the zero-point energy hypothesis which has hitherto been associated with the second form of his theory. Additional evidence in favor of this view including a discussion of the specific heat of hydrogen will be published shortly.

Conclusion.—The complete verification of a natural theory of the asymmetry of the infra-red absorption bands of diatomic gases and the accompanying explanation of the apparent increase in the moment of inertia of the molecule with increasing angular velocity clear up the outstanding difficulties in the theory of the structure of these bands. Consequently there can be no further doubt that it is correct to conclude from the discontinuities in their structure that the angular velocities are distributed among the molecules in the discontinuous manner predicted by the older form of the quantum theory. The proved existence of harmonics in the infra-red spectra of the same gases is almost equally good evidence that the vibrational energy of these molecules is distributed in the same manner.

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[4] Gorton, A. F., *Ibid.*, **7**, 1916, (66).

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